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CONTENTS

The Effect of Various Deoxidizers On Cast Steel 1

Sand Burn-On Without Metal Penetration 8

Russian Production of Steel Castings In Metal Permanent Molds 13

Vibration Technique For Casting Steel 16

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THE EFFECT OF VARIOUS DEOXIDIZERS ON CAST STEEL*

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It is often beneficial in discussing such a subject as the deoxidation of cast steels, to go back to basic principles and definitions in order that all may start with a common understanding. No one has a perfect knowledge of all the principles involved but many have been clearly expounded and proven. All too often, these principles are unknown, poorly understood, or simply ignored by producers of steel castings. If evidence were needed to justify this statement, one might refer to SFSA Research Report No. 38, page 19. In this excellent study, a request was broadcast for typical castings containing hot tears. Of 69 castings received, 53 castings or 77 percent contained Type II inclusions. It can properly be argued that this is not a representative sample of steel castings per se, because they were selected on the basis of hot tears and that Type II inclusions greatly increase the susceptibility of castings to hot tearing. The indictment stands in any case, that too many castings are being made containing Type II inclusions which, in turn, are a result of improper deoxidation practice.

One might say that metallurgy changes from an art to a science when basic principles are applied to the design of practices and to the interpretation of results. It is like comparing a political government ruled by the whims of a dictator to one ruled by law and order under a constitution. Basic laws are immutable and invariant, the same yesterday, today, and tomorrow. While this may sometimes result in frustration, as when an attempt is made to circumvent them, mostly it affords confidence and assurance that if good practice is used consistently good results will be obtained.

It is also pertinent to consider the question, why deoxidize, or why are deoxidizers used? The answer to this can be straightforward and simple. The primary purpose of deoxidation is to obtain castings free of porosity; any other effect is secondary. The ideal casting is completely sound and without porosity. One may tolerate a little porosity at times, but it is never desired.

Deoxidation may be defined as an operation or a reaction in which the oxygen concentration is lowered in a liquid steel. The oxygen content is partially but never entirely eliminated, and the activity of the remaining oxygen is usually decreased to make it less effective. This latter effect is sometimes an important aspect of deoxidation.

It follows naturally that a deoxidizer is an element that has the power to decrease the oxygen content of liquid steel when added to the steel. This is accomplished by combination with the oxygen to form an insoluble compound which precipitates and floats out of the steel bath. To be able to do this, it must have a combining power for oxygen that is greater than that of any element in the steel previously. In other words, it must form a very stable oxide. One way to measure the stability of an oxide is by the free energy of formation of the oxide. For instance, when silicon burns (unites with oxygen) a lot of heat is produced, and this is called an exothermic reaction. The heat released is called the free energy of the reaction and is designated as $\triangle$ F. The free energy is the driving force of a reaction and is here distinguished from $\triangle$ H, the total heat of reaction, because the latter includes heat absorbed or given up as specific heat of the substances. The chemical reaction is:

$$Si + O_2 \longrightarrow SiO_2$$

and when the reaction occurs at 1600 degrees C (2912 degrees F), $\triangle F = -126{,}300$ calories for each gram-molecule of silica formed. Because the heat was given off and lost from the system, it is shown as a negative quantity. In order for the silica to be broken into Si and O_2 again, the same quantity of heat or equivalent energy in the some other form must be furnished and restored to the system. Thus, it is readily seen that the greater the negative value of the free energy the more stable the compound. One with a positive free energy will absorb heat while forming and give off heat during decomposition. The latter compound tends to be unstable.

Table 1 lists the free energies of formation of some of the common oxides of concern in steelmaking reactions. They are for reactions at 2912 degrees F (1600 degrees C) and at 2740 degrees F (1505 degrees C), and all are for one gram-atom of oxygen, for ready comparison. These values give at least an approximate comparison of the stability of these oxides at this temperature. It will be noted that the free energy of formation of any of the other oxides is sufficient to decompose FeO and have some left over. For example, in the reaction:

$$2\ FeO + Si \rightarrow 2\ Fe + SiO_2 \quad \triangle F = -57{,}440 \text{ calories}$$

SiO_2 liberates $-126{,}300$ calories during its formation, however, since the free energy of 2FeO is

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−68,860 calories, this same amount of heat must be absorbed (+68,860) to decompose the 2FeO and allow the reaction to proceed. Therefore, the difference between the heat absorbed and the heat generated is +68,860 −126,300= −57,440 calories, which is the △ F or free energy of the reaction. These oxides, therefore, can form at the expense of FeO. Silica forms in preference to MnO and aluminum has the power to decompose silica. At 2912 degrees F, CO is slightly more stable than SiO_2 which promotes the question of how silicon can stop the carbon boil or prevent the $\underline{C} + \underline{O}$ reaction during freezing.

Fortunately, at the liquidus temperature of a medium carbon steel (2740 degrees F) the free energies are reversed as shown in Table 1. This makes SiO_2 more stable but the difference is not great. This subject will be discussed more later on.

These free-energy relationships do not tell the whole story. They are the driving force of the reaction and indicate whether the reaction is likely to occur, but they do not tell whether it will actually take place, how fast it will go, nor how far it will go. Also, the free energies of elemental substances are substantially higher than when these materials are dissolved in liquid iron. As an example, in the reaction between dissolved carbon and dissolved oxygen

$\underline{C} + \underline{O} \rightarrow CO(g)$ $\triangle F$ 1600°C = +5590 calories,

the free energy of the reaction is thus endothermic in contrast to the data in Table 1.

The strength or potency of a deoxidizer is measured, not by how much oxygen it removes from a liquid steel, but rather by how much it leaves in the steel. The deoxidation reaction, like all chemical reactions, does not go to completion or to exhaustion of the reacting substances. As the reacting substances decrease, the concentration of the products of the reaction increase. Eventually, the free energy of these products create a driving force in the opposite direction equal to the driving force of the reaction, which results in a stalemate called equilibrium. For a clear understanding of the phenomenon of deoxidation, it is necessary to have some conception of the meaning and importance of the "law of mass action" and the "equilibrium constant". These are expressions of the same thing. The law of mass action states that when a reaction reaches equilibrium at a constant temperature the product of the active masses on one side of the chemical equation when divided by the product of the active masses on the other side of the equation is a constant, regardless of the amounts of each substance present at the beginning of the reaction.

TABLE 1—Free Energies of Formation of Some Common Oxides When The Reaction Takes Place at 2912 degrees F (1600 degrees C) and at 2740 degrees F (1505 degrees C). For Ready Comparison They Are All on The Basis of The Reaction of One Gram Atom of Oxygen. (Values Calculated From Tables of Free Energies in Chapter 14 of "Basic Open Hearth Steelmaking", 1951)

Reaction	△ F Per Gram Atom O at 2912°F (1600°C)	△ F Per Gram Atom O at 2740°F (1505°C)
Fe (l) + ½ O_2 → FeO (l)	−34,430	−35,630
Mn (l) + ½ O_2 → MnO (s)	−57,000	−59,000
C (s) + ½ O_2 → CO (g)	−65,900	−64,100
½ Si (l) + ½ O_2 → ½ SiO_2 (s)	−63,150	−65,400
⅔ Al (l) + ½ O_2 → ⅓ Al_2O_3 (s)	−85,500	−88,000
½ Ti (s) + ½ O_2 → ½ TiO_2 (s)	−68,550	−70,650
½ Zr (s) + ½ O_2 → ½ ZrO_2 (s)	−86,750	−89,000

For example, in the deoxidation of liquid steel with silicon when the reaction

$$SiO_2 = \underline{Si} + \underline{2O}$$

reaches equilibrium (which occurs very quickly) then

$$\frac{[\%\ Si]\ [\%\ O]\ [\%\ O]}{\%\ SiO_2} =$$

$$\frac{[\%\ Si]\ [\%\ O]^2}{\%\ SiO_2} = \text{a constant} = K.$$

The SiO_2 is instantly precipitated and in this form a little is just as effective as much. The quantity, therefore, is unimportant and this factor can be omitted giving merely:

$$[\%\ Si]\ [\%\ O]^2 = K$$

for any given temperature. K is the equilibrium constant.

It means, of course, that there is a very definite and reproducible relationship between the silicon content and the oxygen content when silicon is the principal deoxidizer. This is equally true for any other deoxidizer. As the silicon content goes up, the oxygen content must go down to keep the product constant. Such emphasis on a simple fact seems warranted because of certain statements, possibly prompted by wishful thinking, that, somehow by slight-of-hand or other means, deoxidized steels with high oxygen content can be produced and that such steels should have superior properties. A deoxidized steel is a low-oxygen steel and the greater the degree of deoxidation the lower the oxygen content. The relation of various deoxidizers to oxygen content is shown in Figure 1.

Among the deoxidizers for cast steel, both carbon and hydrogen play an important part. Carbon, of course, is the principal strengthening constituent in steel and is used primarily for that purpose. Hydrogen on the other hand is an insistent interloper, never wanted, and efforts are usually made to keep its con-

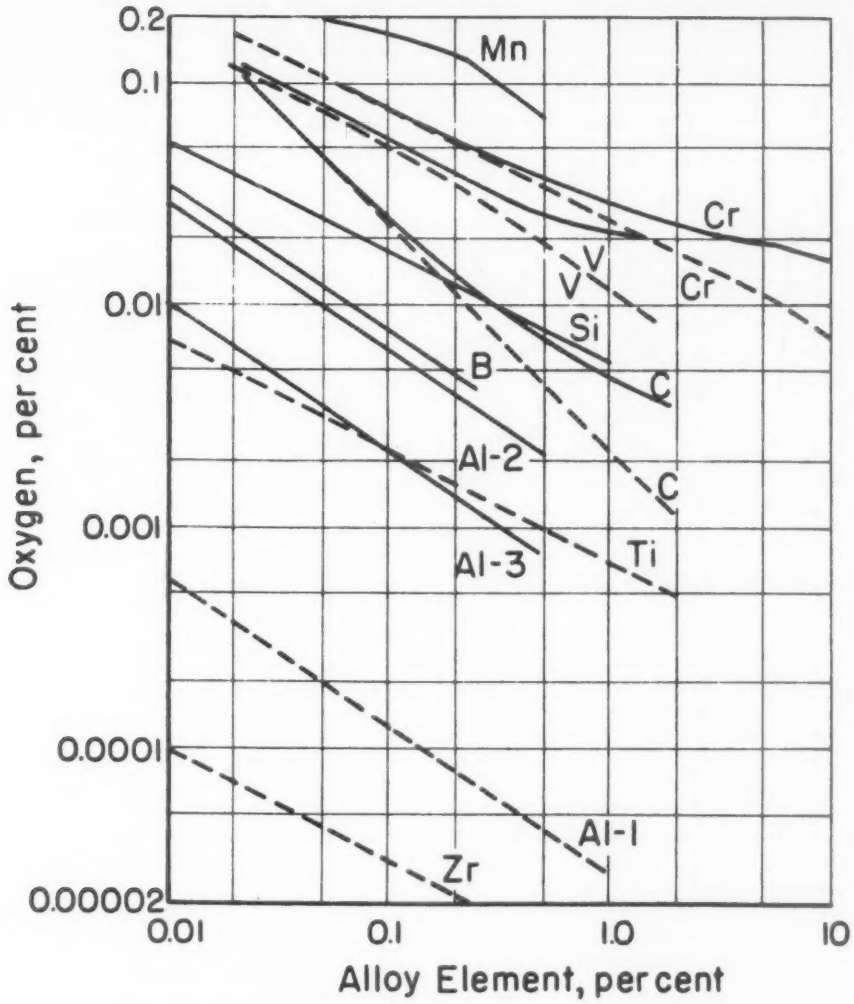

Figure 1—Summary of information on deoxidation. Solid lines, observed concentration; broken lines, oxygen activities.

Note discrepancy in case of aluminum: Al-1, calculated: Al-2, Hilty and Crafts[84]; Al-3, Wentrop and Hieber[85].

tent as low as possible. Both carbon and hydrogen are unique among deoxidizers in that the products of deoxidation are gases:

$$\underline{C} + \underline{O} \rightarrow CO(g)$$

$$2\underline{H} + \underline{O} \rightarrow H_2O(g).$$

The prime purpose of deoxidation, as practiced, is to prevent these elements from functioning as deoxidizers during freezing of a cast steel, and thus avoid porosity.

Carbon-Oxygen Reaction

Silicon is the great, common deoxidizer for cast steel and is almost universally used even though other materials are also used. As may be seen from Figure 1, silicon and carbon appear to be roughly equivalent as deoxidizers and thus silicon could be expected to give questionable protection against the carbon-oxygen reaction. It is known from experience, however, that it does give such protection and a closer study will show the reason why. Data are plotted in Figure 2, to show the equilibrium relations of oxygen with silicon, carbon, and hydrogen. Two lines are shown for silicon, one to represent the silicon-oxygen equilibrium at an operating temperature of 3000 degrees F and the other at 2740 degrees F, which is about the liquidus temperature for a medium carbon steel. It is readily apparent that silicon becomes a better deoxidizer as the temperature drops and is far more efficient at the freezing temperature of steel than at the operating temperature when it is added.

Two lines also are drawn for the carbon-oxygen equilibrium at the same two temperatures and show

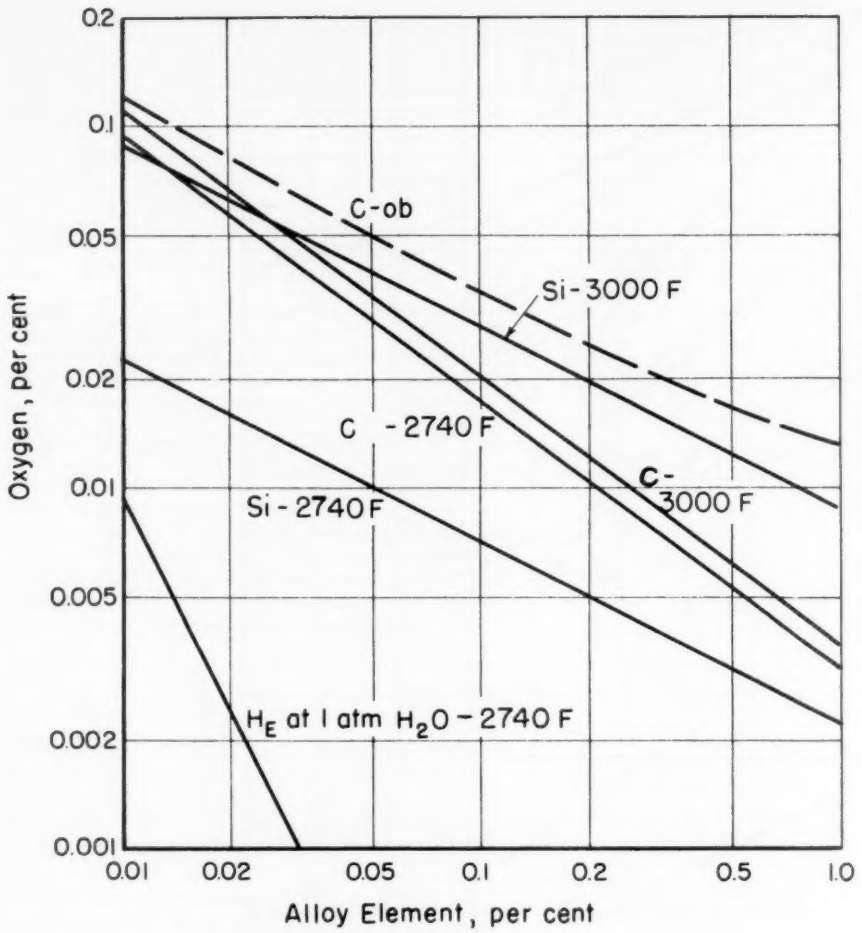

Figure 2—Equilibrium relations of carbon, silicon and hydrogen with oxygen in liquid steel. C-ob, average of carbon and oxygen contents of oH steel. C_E, C-O equilibrium with one atmosphere CO. H_E, H-O equilibrium with mixture of H_2 and H_2O, partial pressure of H_2O one atmosphere.

that this equilibrium is affected only slightly by temperature changes. For equilibrium at 3000 degrees F, it will be noted that, for equivalent concentrations, carbon is a better deoxidizer than silicon at any content over about 0.025 percent. How then, can silicon kill the boil; i.e., stop the C-O reaction?

As has been pointed out, carbon differs from silicon in having a gaseous reaction product, CO. When a reaction involves a gas, the equilibrium expression must include a figure for the pressure of this gas. The standard equilibrium for the carbon-oxygen reaction is at one atmosphere pressure of CO. During the oxidizing period of a heat, this equilibrium is never reached. The ferrostatic head of the liquid steel and the resistance to bubble formation[1] require escaping pressures greater than one atmosphere for the evolution of CO from molten steel. The dashed line of Figure 2 (carbon observed) gives the mean values of a large number of samples taken from an open-hearth near the finishing period of the heat and shows the actual relation between carbon and oxygen. This can be considered a pseudo equilibrium, or better, equilibrium at higher pressures of CO varying from about 2 atmospheres at 0.1 percent carbon to 5 atmospheres at 1 percent carbon. Thus, even at 3000 degrees F, silicon can stop completely the carbon boil in a steel bath. For example, with 0.2 percent carbon an addition of 0.1 percent silicon would suffice. At somewhat higher temperatures, silicon is impotent to stop the carbon boil and greatly overheated converter heats have been known to finish with low carbon and silicon contents as high as 1 percent.

At the solid-liquid interface of a freezing steel, the conditions for bubble formation are much more favorable and, apparently gas pressures closer to one atmosphere are effective. Under these conditions, much lower oxygen contents are necessary to prevent evolution of CO, but an examination of the equilibrium curves for silicon and carbon for 2740 degrees F will show that silicon is adequate for the task. For ex-

ample, 0.5 percent silicon is sufficient for any carbon content up to about 1.0 percent. At such high carbon contents, the margin of protection is almost nil, and dendritic segregation during freezing could easily upset the balance. Experience indicates that it is advisable to rely on a stronger deoxidizer than silicon for very high-carbon steels to avoid porosity.

Hydrogen-Oxygen

Figure 2 also contains a curve showing the equilibrium relations of hydrogen to oxygen in liquid steel which is also in equilibrium with a mixture of H_2 and water vapor in which the partial pressure of the water vapor is one atmosphere. On this basis, for equal weight percents, hydrogen is a better deoxidizer than silicon at 2740 degrees F. For example, both 0.2 percent silicon and 0.015 percent hydrogen are in equilibrium with 0.005 percent oxygen. This is hardly a fair comparison, however, because hydrogen is such a light element, and 0.4 atomic percent silicon is equivalent to 0.83 atomic percent hydrogen. Thus, atom for atom, silicon is twice as strong a deoxidizer as hydrogen. It is true also that 0.015 percent hydrogen or 150 parts per million is a vastly higher concentration than is ever expected in liquid steel, and it should be clear why a hydrogen boil analogous to the carbon boil is impossible.

The equilibrium content of oxygen in a medium carbon steel containing 0.5 percent silicon and at the liquidus temperature is about 0.003 percent. For hydrogen to generate an escaping pressure of one atmosphere of H_2O, it would have to be present in a concentration of 0.018 percent or 180 parts per million. Numerous analyses have established the expected hydrogen content in cast steel, at the time of pouring, in the range of 5 to 15 parts per million. At first thought, 180 ppm seems like an impossibly high concentration. When the high initial rate of freezing of a light section casting is considered, the sharp drop in hydrogen solubility during freezing and the rapid diffusion rate of hydrogen at such high temperature, it is logical to expect an appreciable dendritic segregation of hydrogen at the solid-liquid interface of the freezing skin. If the steel were to be poured with a hydrogen content of 9 ppm, a concentration of 20 to 1 would bring it to 180 ppm. This does not seem impossible for such a material. This concentration, in the case of a green sand casting, can be markedly bolstered by hydrogen generated at the surface by the reaction

$$Fe + H_2O(g) \rightarrow FeO(s) + 2\,H.$$

The solid FeO stays on the surface while the hydrogen filters through the frozen skin to increase the concentration at the solid-liquid interface. When the content gets high enough, it is believed that porosity is initiated by the formation of a tiny bubble of water vapor. Also, H_2O does not have to work alone, and it may be the combined partial pressures of H_2O and CO that start the bubble.

The hydrogen itself would exert an escaping pressure of 53 atmospheres at a concentration of 180 ppm. The pertinent question is, with such a pressure, why cannot the hydrogen initiate bubble formation without the aid of oxygen? No good answer can be given to this question, yet. Evidence indicates that oxygen plays an important role. For example, a silicon-killed steel poured into a green sand mold may develop porosity. If a small addition of aluminum is made to the same steel, often as little as 0.01 to 0.02 percent, which is then poured into an identical green sand mold, the casting will be free of porosity. The essential difference is the active oxygen content of the liquid steel. Although hydrogen appears unable to initiate bubble formation, the high pressure will insure rapid growth when once started.

The solubility of nitrogen in steel also must be stated in relation to the pressure of an atmosphere of that gas. It exerts an escaping pressure, therefore, and, though like hydrogen it apparently cannot start bubble formation, it will precipitate into any bubble formed and help it to grow.

Side Effects of Deoxidizers

Thus, deoxidizers are used to control porosity in castings, but the law of compensation applies here as in most other things, and deoxidation is not an unmixed blessing. In other words, you have to pay for what you get. In view of this, it behooves us to select the deoxidizer which gives the best bargain.

The foregoing concludes that an element is a deoxidizer because it is chemically active and forms a stable oxide. Such an element, however, is very likely to form other stable compounds like nitrides, sulfides, and carbides. This introduces side effects which may be good, bad, or indifferent, but which must be considered when evaluating a deoxidizer. An antibiotic may be an excellent germ killer, but if it also kills the patient it must be discarded.

There is one very important side effect that is common to all strong deoxidizers, so common in fact that it must be regarded as a function of deoxdiation itself. It is the conversion of the large globular Type I sulfides to the eutectic Type II sulfides with resultant detriment to the ductility of the steel. The Type II sulfides may be produced by appropriate additions of aluminum, zirconium, titanium, misch metal, or magnesium[2] in medium carbon steels and by silicon in steels containing over 1 percent carbon as reported by Christopher[3]. When deoxidation is uniform or when the deoxidizer is uniformly dispersed in the steel, the transition from Type I to Type II is abrupt and complete and occurs at a definite level of deoxidation. Thus, the appearance of Type II sulfides can be used as a qualitative measure of deoxidation and the ability of an addition to produce Type II sulfides as a measure of its deoxidizing potency.

The characteristics of the various types of sulfides and the probable mechanism of their formation has

been described elsewhere[4] and need not be detailed here. Suffice it to say that deoxidation largely controls the characteristics of the inclusions, and that inclusion type and quantity are the most important factors governing the mechanical property variations in the steel. For a given type of inclusion, the ductility will vary inversely with the total quantity. The importance of type is shown by figures from Research Report No. 39[5]. Of 150 steels studied, the proportion of those with room-temperature Charpy values over 40 foot-pounds were related to inclusion type as follows:

Steels with Type I sulfides 94 percent
Steels with Type III sulfides 80 percent
Steels with Type II sulfides 5 percent.

For reduction of area values in tension greater than 40 percent, they were:

Steels with Type I sulfides 99 percent
Steels with Type III sulfides 89 percent
Steels with Type II sulfides 40 percent.

While it is obvious that the Type I is best and the Type II worst, there is not a simple correlation of inclusion type with ductility because of the influence of other factors such as soundness, composition, and strength level. Also, a low sulfur steel with Type II sulfides can have better ductility than a high sulfur steel wih Type I sulfides.

One of the important side reactions is the combination of deoxidizers with the sulfur content of the steel and the effect of the sulfides so formed on the properties of the casting. Table 2 shows the free energies of formation of some metal sulfides at 2740 degrees F which give some indication of the likelihood of their formation in steel at that temperature.

TABLE 2—Free Energies of Formation of Some Metallic Sulfides at 2740 Degrees F (1505 Degrees C)

Reaction	△ F at 2740 F (1505 C)
$Fe\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow FeS$	−16,220 calories*
$Mn\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow MnS$	−34,700 calories*
$Ca\ (g) + \frac{1}{2}\ S_2\ (g) \longrightarrow CaS$	−85,600 calories*
$\frac{1}{2}\ Si\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow \frac{1}{2}\ SiS_2$	+ 2,600 calories*
$\frac{2}{3}\ Al\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow \frac{1}{3}\ Al_2S_3$	−13,800 calories*
$Ti\ (s) + \frac{1}{2}\ S_2\ (g) \longrightarrow TiS$	−45,000 calories**
$Ce\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow CeS$	−98,000 calories†
$\frac{2}{3}\ La\ (l) + \frac{1}{2}\ S_2\ (g) \longrightarrow \frac{1}{3}\ La_2S_3$	−72,000 calories††

* "Basic Open Hearth Steelmaking"

** Calculated from data in "Metallurgical Thermochemistry", by G. Kubaschewski and E. LL. Evans.

†"The Thermodynamics of Substances of Interest in Iron and Steelmaking. III Sulphides" by F. D. Richardson and J. H. E. Jeffes, Journal Iron and Steel Institute (London), 165-175 (June, 1952).

†† Calculated from data in "High Temperature Technology" by J. E. Campbell, John Wiley & Sons, Inc., 190 (1956).

For example, MnS has twice the free energy of FeS and would definitely take precedence over the latter. The very high free energy of CaS indicates the potentiality of calcium as a desulfurizer. On the other hand, SiS_2 will not form in the presence of iron at freezing temperatures, while Al_2S_3 is not likely to form although it has been tentatively identified[6] in steels containing abnormally high contents of both sulfur and aluminum. The calculated figure for the free energy of formation for TiS appears to be reasonably reliable. Titanium reacts violently with sulfur and forms a highly stable compound. It appears to be readily capable of displacing sulfur from MnS. Cerium sulfide is more stable than calcium sulfide while lanthanum sulfide is only slightly less stable. Both CeS and La_2S_3 are considerably less soluble in liquid steel than FeS and MnS.

Most strong deoxidizers also combine avidly with nitrogen, and in Table 3 are shown the free energies of formation of some nitrides at 2740 degrees F (1505 degrees C). Iron nitride, which is not shown, is not stable at this temperature, but aluminum, titanium, zirconium, cerium, and lanthanum form very stable nitrides. Boron nitride is somewhat less stable. It will be noted where comparisons can be made, that the order of stability is, oxides first, nitrides second, and sulfides third. It does not follow, however, that the elements which form the most stable oxides also form the most stable sulfides. Because of the instability of iron and manganese nitrides at the freezing temperature of steel, nitrogen, when present, contributes importantly to the porosity of steel by precipitating into any bubbles formed. The high stability of deoxidizer nitrides is therefore important, and deoxidation is also denitridation, although the nitrogen content of the steel is not usually lowered.

Characteristics of Deoxidizers

A tremendous amount of work has been done in the search for the best deoxidizers and the best deoxi-

TABLE 3—Free Energies of Formations of Some Nitrides at 2740 Degrees F (1505 Degrees C)

Reaction	△ F at 2740 F (1505 C)
$Al\ (l) + \frac{1}{2}\ N_2 \longrightarrow AlN$	−26,000 calories*
$Ti\ (s) + \frac{1}{2}\ N_2 \longrightarrow TiN$	−40,000 calories*
$Zr\ (s) + \frac{1}{2}\ N_2 \longrightarrow ZrN$	−42,000 calories*
$B\ (l) + \frac{1}{2}\ N_2 \longrightarrow BN$	− 9,000 calories*
$Ce\ (l) + \frac{1}{2}\ N_2 \longrightarrow CeN$	−32,500 calories†
$La\ (l) + \frac{1}{2}\ N_2 \longrightarrow LaN$	−27,600 calories†

* Pearson, J. and Ende, U. J. C., "The Thermodynamics of Metal Nitrides and of Nitrogen in Iron and Steel", Journal Iron and Steel Institute, September, 1953.

† Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy", VIII The Thermodynamic Properties of Metal Carbides and Nitrides, Bureau of Mines Bulletin 407.

dation practices. Among this is 5 years spent by Battelle under the sponsorship of the SFSA. In this work, practically every promising and available element was tested for its potentialities as a deoxidizer or desulfurizer. Some metals, such as beryllium and thorium, for example, were not studied for economic reasons, even though they might be excellent deoxidizers.

The method of evaluating a potential deoxidizing element was to determine first, does it deoxidize? That is, does it adequately suppress porosity, and second, what are its side effects? Practically all the work was done on a low-alloy high-strength steel. Two criteria were used to determine deoxidizing powers: one indirect and the other direct. In the indirect method, a section of a standard casting was examined under the microscope for sulfide characteristics. If an element could not convert Type I to Type II sulfides, it was not regarded as a strong deoxidizer. For the direct test, a standard angle casting was made in green sand molds of various moisture contents and these castings were examined for pinhole porosity. Deoxidation with aluminum was the standard for comparison. Sulfur analyses on samples taken before and after the addition determined the desulfurizing ability of the material.

The results and conclusions of this work have been written very comprehensively in SFSA Research Report No. 39, which has just recently been distributed. On the background of this work and other similar studies, some general conclusions regarding deoxidation and desulfurization can be made, keeping in mind that general statements are not likely to be highly accurate for all conditions.

The matter of desulfurization by alloy addition can be disposed of very quickly. The only effective desulfurizers found were the rare earths, used in the form of misch metal. When enough is used to give appreciable lowering of the sulfur content, however, the steel is loaded with an undesirable type of inclusions. They seem to be a mixture of oxides, sulfides, and nitrides. It is also expensive for this purpose. The only practical and economical way to desulfurize steel is by treatment with a basic slag.

Manganese

Of all the materials classed as deoxidizers, manganese can be considered as the one most nearly indispensable. It is used in practically all steels, even when silicon is omitted.[7, 8] By itself, it is a relatively weak deoxidizer, but its presence makes silicon and aluminum better deoxidizers than they would be alone[7, 8]. It is a potent alloying agent and can improve the mechanical properties and the hardenability of a steel. But, it has one great virtue which would cause it to be used even in the absence of any other merit and that is its ability to form a stable, high-melting compound with sulfur.

When sulfur occurs in manganese-free iron, it forms FeS, which has a melting point of 2190 degrees F, but FeS forms a eutectic with iron which freezes at 1805 degrees F and which contains about 30 percent sulfur. During freezing of the iron, this eutectic is deposited in the primary grain boundaries and dendritic interstices as a pale, canary yellow film, which constitutes a continuous phase. A steel containing such a film formation will be extremely hot-short, and brittle when cold.

MnS is notably more stable than FeS, as will be noted in Table 2, and, when manganeses is added to a steel in an amount in atomic excess of the sulfur content, it virtually preempts the latter and forms MnS. An addition of 4 or 5 times the weight percent of sulfur will insure that the sulfides formed will be predominantly MnS. The freezing point of MnS is 2930 degrees F. It is soluble in liquid steel, though not so soluble as FeS, and does sometimes precipitate as the sulfide portion of a sulfide-iron eutectic, that is, as Type II inclusions. In normal steels containing ½ percent or more of manganese, the sulfides are essentially MnS whether they are classed as Type I, II, or III.

Aluminum

After manganese and silicon, aluminum is the most widely used deoxidizer. It is not used as an alternative but as a supplement to the first two elements. It has a number of advantages to account for its wide use, such as low cost, ready availability, and stability in storage. It is one of the most powerful of the deoxidizers available, being rivaled only by zirconium. Because of its high potency as a deoxidizer, only small additions are required to give quite effective deoxidation. Such small additions, however, may lead to formation of Type II inclusions and result in poor ductility. This effect, which has been known for many years, has tended to give aluminum a bad reputation as a deoxidizer, even to the extent of calling it a poisoner of steel. It has been found, however, that an addition of aluminum somewhat greater than that required for complete deoxidation can cause a further change in the sulfides to the Type III. This gives a considerably enhanced ductility as compared to the Type II inclusions but never quite so good as with the Type I. Such use of a judicious excess of aluminum has taken the onus from it to a considerable extent, but it is still regarded with suspicion in some quarters.

Unfortunately, the proven benefits of using an excess of aluminum have sometimes led to excessive use of aluminum, and when used in quantities which give residual contents above 0.06 percent, a less favorable type of sulfide inclusion is formed, tending more to intergranular films than the ideal Type III inclusions.

Aluminum present in excess of that required for deoxidation tends to unite with any nitrogen present to form aluminum nitride (AlN). AlN has a limited solubility in solid steel and this solubility varies with temperature. As the temperature of a casting cools from the freezing point, the saturation with AlN will be reached at some temperature, after which it will

precipitate. The preferred location for such precipitation is primary grain boundaries, probably because both aluminum and nitrogen are present at these locations in the highest concentration as a result of dendritic segregation. When present in sufficient quantity, AlN produces great brittleness and low strength and causes the steel to break with an intergranular type of fracture often called the "rock candy" fracture.

Titanium

Titanium may properly be considered as a superdeoxidizer for steel and is presently available either as fairly pure metal or as a constituent of some complex proprietary alloy. It is not quite so strong a deoxidizer as aluminum, but when added to steel in quantities greater than about 0.015 percent, Type II sulfides will be produced. Unlike aluminum, a further increase in the residual titanium does not cause a change to Type III inclusions but produces a more extreme eutectic type of sulfide. As the titanium content increases, the sulfides change from the characteristic dove gray color of manganese sulfide to a light tan color which is thought to be titanium sulfide. Thus the improvement in ductility that accompanies the formation of Type III sulfides cannot be accomplished with titanium.

Titanium nitrides are far more stable than aluminum nitrides and also seem to be completely insoluble in solidified steel. Because of this, any titanium present in excess of that required for deoxidation will combine with nitrogen and form nitrides which precipitate during freezing and appear as salmon or pink colored cubic crystals. Titanium also forms very stable and insoluble carbides, and the nitrides often contain some carbide.

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SAND BURN-ON WITHOUT METAL PENETRATION

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The British Steel Castings Research Association has recently issued a report, entitled "Some Iron-Oxide/Refractory Interactions in Steel Founding", containing some results of work sponsored by the Association at Cambridge University aimed at an understanding of the causes for the adherence of molding sand to steel castings. The following is an extended summary of the first portion of this report which deals with sand adherence without metal penetration.

Introduction

The problem of "burn-on" or sand adherence to steel castings has received much attention because of health hazards and economic considerations associated with removal of the adhering material. Many theories of the causes of adherence have been advanced and lately the important part played by metal penetration of the sand of the mold has been demonstrated by several workers. However, metal penetration cannot account for all cases of sand adherence. Foundrymen are well aware of the adherence of sand to solid metal; for example, in a case where ingots, cast in conventional metal molds, were knocked out while very hot on to the sand floor of the foundry, severe sand adherence on the lowest faces was found.

Since chemical reactions occurring at the mold-metal interface may well influence the incidence of "burn-on", an attempt has been made in this investigation to obtain a more complete understanding of the interaction of iron oxide and sand at the mold-metal interface and especially to determine if, and under what conditions, severe sand adherence to the metal can occur without metal penetration.

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Several workers have examined the problem of sand adherence to steel castings in the foundry. From their work practical remedies for the improvement of surface finish of castings have resulted, although reactions, especially chemical, at the mold-metal interface are not yet fully understood.

Goodale[1] postulated the formation of an "oxide slag" which penetrated between the sand grains of a mold on account of its high fluidity at steelfounding temperatures, followed by a secondary chemical reaction between the iron oxide and the silica. He considered that the nature of this reaction was dependent on temperature and, while reporting little experimental data, gave illustrations indicating the progress of possible reactions. He accounted for the presence of free iron in the penetrated sand by suggesting reduction of the "oxide slag" by carbon in the molding materials.

Dierker[2] referred to the possibility of the formation of ferrous silicate at the mold face. Chemical analysis of the scale from a casting surface showed quantities of iron compounds to be present, but the only evidence offered for the presence of a silicate was the characteristic green coloration.

Vaska[3] observed that metallic oxides could greatly reduce the fusion temperatures of molding materials, but thought that adherence was due to the metal remaining molten long enough to penetrate into pores and cracks. The presence of a fused layer of viscous slag at the mold-metal interface could hinder penetration and thereby cut down the degree of adherence.

Caine[4] supported the metal-penetration theory and the part played by viscous slags in the prevention of penetration. He also gave a mechanism for the enlargement of voids by fusion of finer silica particles and colloidal matter in the sand. The mechanism of sand adherence was treated as a purely physical problem and no importance was attached to chemical reactions. In later work Ljunggren[5] and Holmquist[6] supported Caine's findings and made observations as to the significance of the permeability, mean grain size and sintering point of the molding materials.

Dietert, Doelman and Bennett[7] demonstrated that reactions could take place well below the solidification temperature of the casting, down to a temperature of 1796 degrees F. They recognized two effects: (1) metal penetration and (2) oxide penetration. The investigation dealt only with (2) and gave a hypothetical series of reactions, stating that the products of "oxide penetration" were FeO, Fe_2O_3, a trace of Fe_3O_4, iron silicate(s) and free iron with carbon at a higher percentage than that of the casting.

Taylor and Morey[8] described the prevention of a fused black layer next to a casting by bleeding the casting shortly after pouring to leave a skin between 1/32 and 1/16 inch thick. Under these conditions of rapid chilling of the mold-metal interface, firm sand adherence occurred, whereas if the casting was allowed to cool in the normal way, the fused black layer formed and peeled cleanly. The conclusion drawn was that the fused layer formed after metal solidification and that it improved the peeling properties of the sand. These workers stated that, although they did not believe the term "oxide penetration" fully described the phenomenon and despite the reference by Dietert and his co-workers to the presence of free iron, they themselves had never found that metal penetration was a feature of the tests described by Dietert. Jones[9], however, reported a test in which a casting made in a green sand mold was bled immediately after pouring and found that the solidified shell was fairly easily stripped from the mold walls.

Hoar and Atterton[10] pointed out that the work hitherto had been concerned almost entirely with observations of penetration in practical castings and that most of the hypotheses advanced had been supported by experimental evidence. These authors carried out experiments in the laboratory largely concerned with the physical factors affecting metal penetration and, therefore, will not be dealt with here.

Savage and Taylor[11], using an extension of the methods of Taylor and Morey, investigated the formation of fayalite ($2FeO.\ SiO_2$) in sand molds used for making steel castings. This material was found to be the only product of reactions occurring at mold-metal interfaces in both laboratory and foundry castings. These workers gave X-ray diffraction data for the synthetic fayalite produced in their experiments. They also noted that burn-on of sand was often worse in the case of small thin castings than in that of somewhat larger castings, and suggested that this might be due to "lack of time and/or temperature" (presumably rapid cooling and/or low thermal capacity).

Pettersson[13] observed that the formation of a silicate slag appeared to take place after solidification of the metal and expressed the opinion that the effect of such slag formation in mechanically preventing penetration had been much exaggerated.

Gertsman and Murton[14] found that a fused layer of mold material was produced next to the molten metal by using a sufficiently high pouring temperature. The presence of this fused layer did not prevent penetration. For a given casting head there was a critical temperature below which there was little effect on the extent of penetration by further reduction in the temperature of pouring.

The work of Hoar and Atterton has been extended to determine the influences of binder content, degree of ramming and sintering, and the effects of mold washes on the penetration of molten metals into compacted sand mixes. Results for the effect of mold washes indicate that viscous fluid formation at

the mold-metal interface may be of practical use in minimizing penetration.

The use of practical foundry techniques has prevented most workers from accurately analyzing the separate effects of physical and chemical reactions at the mold-metal interface, but since the discovery that metal is often present between the grains of adhering sand, it has been generally concluded that the major proportion of sand adherence is caused by metal penetration. However, there are undoubtedly cases of adherence where metal penetration is absent and indeed impossible, as when sand adheres to solidified metal. Hoar and Atterton eliminated chemical reactions between the metal and mold material and examined the purely physical interactions and their significance in the problem of sand adherence: the present work has been planned as a direct corollary to that work, using a similar laboratory approach, but eliminating physical penetration and instead studying chemical reactions. Four sands were used: two silica sands, a Norwegian olivine and a zircon sand.

Apparatus

Hoar and Atterton[10] state that an apparatus used for investigating reactions which occur at the mold-metal interface should reproduce certain conditions, of which the following are relevant to the present work:

1. The sand or other refractory should be heated by contact with the molten metal.

2. The metal should be in motion.

In addition it was necessary to ensure, in the present work, that

3. the pressure across the sand-metal interface should be less than that which would cause molten metal to penetrate between the grains of sand.

The Interaction of Molten Oxide on Molten Iron With Sand

Dry silica, zircon or olivine sands dropped onto the surface of molten unoxidized iron did not react with the iron, and the sands were easily brushed off from the cooled solidified metal.

However, if the metal was oxidized and sand was dropped onto its surface, the molten oxide penetrated upwards into the heaped sand by capillarity, forming a cake of thickness proportional to the amount of oxide present. The sand oxide cakes peeled easily from the solid iron.

Silica sand bonded with bentonite gave clean peeling cakes, even though they were penetrated with oxide. The quantity of oxide present determined only the thickness of the penetrated sand and not its peeling properties. The temperature of the metal before oxidation was varied from 2820 to 3000 degrees F without significant effect.

The mechanism of penetration of the oxide appears to be as follows. The large degree of superheat of the oxide (390 - 750 degrees F) enables it to penetrate the sand almost instantaneously. The hot penetrating oxide cracks the sand grains and may carry some of the smaller particles along with it. The oxide which has penetrated furthest, solidifies rapidly in comparison with that nearer the melt, with little, if any, interaction with either the small particles or the sand grains themselves. Near the metal-sand interface the oxide remains molten for a period long enough for it to attack both the particles and the larger grains, leading to the separation, on cooling, of a third phase formed as a result of this interaction. Silica is attacked readily, olivine and alumina less readily and zircon not at all. However, the formation or otherwise of a third phase does not affect the characteristics of the peeled metal surface.

A thin layer of oxide was present between the sand-oxide cake and the metal, when the cake peeled cleanly from the solidified metal pellet. The separation of the cake from the metal always occurred within this oxide layer, which adhered partly to the metal surface and partly to the surface of the cake. Where there was adherence of the cake to the metal, there was no evident formation of such a layer. Thus the nature of this layer and the manner of its formation seem to be important in determining whether or not adherence occurs.

No fayalite was found in experiments with silica sand in the thin oxide layer on the surface of the cleanly peeled pellets, and there was only slight interaction at the oxide-sand-oxide cake interface. Thus the oxide layer must have formed after the metal had solidified and parted from the cake, leaving a contraction gap. The oxide-penetrated cake would be substantially solid and supported by its solidified upper surface, thus allowing the formation of a contraction gap.

Any liquid oxide formed after solidification of the metal, but before the metal temperature fell to about 2500 degrees F, would remain on the surface of the metal. It would not be removed as was the bulk of oxide which was originally present, by the sponge action of the heaped and compacted sand.

The addition of cold sand to the surface of the molten metal at a temperature near that of the liquidus of the metal would be sufficient to cause immediate solidification of the metal and no contraction gap would be formed. A firm adherence would result in such cases between the sand-oxide cake and the metal, and no thin layer would form between the cake and the metal.

Examination of adhering sand-oxide cakes showed that there were small metal prongs extending from

the metal surface into the oxide-penetrated sand cake and resulting in the interlocking of the two dissimilar materials.

The Interaction of Molten Oxide on Solid Steel With Sand

Results obtained when the metal remained solid and only the oxide was molten were markedly different from the results when the metal also was molten. Studies were made with solid steel heated under oxidizing conditions to temperatures below the liquidus of the steel.

Adhering sand-oxide cakes were obtained with silica, olivine and alumina. Zircon produced an oxide cake which separated from the metal surface on cooling. In all cases the thin layer of oxide found when molten metal was employed, was absent when solid metal was oxidized.

There was no interaction between silica sand and oxides if heating temperatures were below the melting point of iron oxide.

A study of the adhering layer showed that the sand-oxide cake was anchored to the metal surface by small prongs of metal extending into the cake.

The oxidation of the solid metal surface produced pits which were then filled with liquid oxide. This penetration of the liquid oxide into the metal gave the cooled specimen the appearance of metal prongs extending into the slag cake. Figure 1 shows the penetrated layer. The liquid oxide apparently reacts with silica, and fayalite is formed in and around the pits produced by oxidation.

The appearance of the interface is similar to that found in cases of metal penetration into sand molds, though the metal penetration prongs are much larger. However, the phenomenon is the reverse of metal penetration: *it is oxide penetration into the metal.* Metal penetration can occur only when the metal is molten, oxide penetration can occur only when the metal is solid. This explains the fact that if a casting is knocked out very hot, there is often less adherence of the sand mold than that found when the casting is allowed to cool in the mold. In the absence of interaction between the refractory and iron oxide, the peel of the sand-oxide cakes is similar to that of the oxide alone. This is the case when zircon is employed as the molding media.

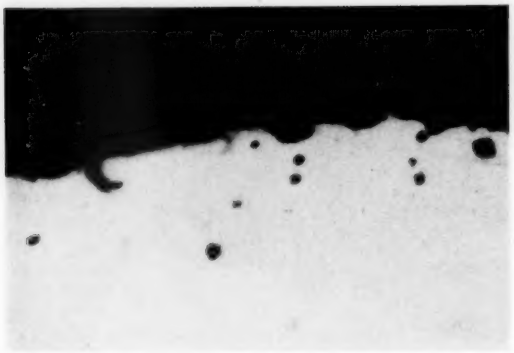
The Formation of Pits and Prongs by Oxidation and the Mechanism of Sand Adherence

The solid metals used in this investigation have all shown an irregular surface on oxidation with the formation of metal prongs, oxidation pits, and internal pockets of oxide in the metal below the surface. Some of the photomicrographs of sections through metal-mold and metal-oxide interfaces, published by other workers, also show these phenomena, but no attention has been drawn to any significance they may have in determining oxide or sand adherence to the metal. Formerly, attention has been primarily directed to the friability and porosity of the scale formed.

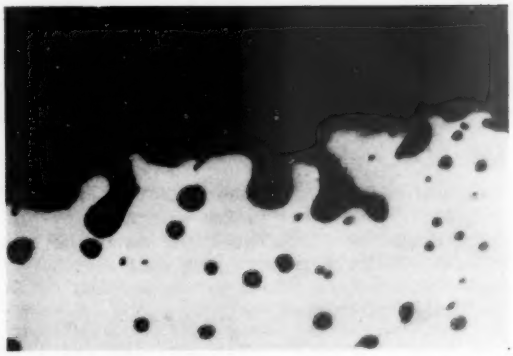
Figure 1—Section through metal/oxide interface, showing penetration of oxide into the metal (metal, light; oxide, gray). 500x

The present microscopical investigation is in agreement with these previous observations, and further indicates that formation of the irregularly oxidized surface may occur in the following way. Oxidation of a smooth metal surface, at elevated temperatures, produces a surface layer of oxide and, at the same time, a layer of oxide particles is produced below the surface of the metal by diffusion of oxygen into the metal. The size and numbers of these oxide inclusions increase with time and, as oxidation of the surface proceeds, some inclusions link up with the surface to form pits. As oxidation proceeds further, other pockets of oxide link up with the pits, producing an even more irregular metal-oxide interface. This process eventually reaches a steady state with the prongs of metal being destroyed as new pits are formed. A sequence of the changes occurring in the metal-oxide interface formed from an originally smooth surface by progressive oxidation is shown in Figure 2; this is manganese steel, which readily forms large inclusions of oxide and demonstrates the phenomenon most clearly. Evidently, the effect can only occur when the metal is solid, although the oxide formed may be either liquid or solid.

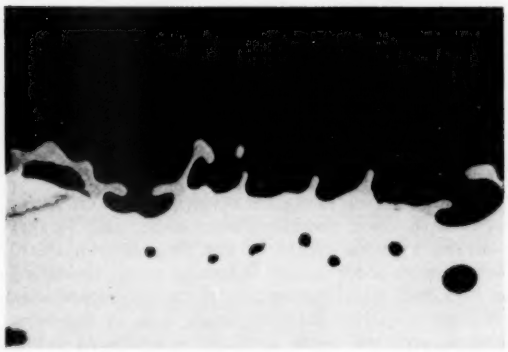
Sand (e.g., silica) brought into contact with the metal under these conditions is penetrated by and reacts with the liquid oxide to produce a fluid slag which wets both the irregular metal surface and the oxide-penetrated sand. The solidified slag is mechanically strong and keys onto the metal surface, causing adherence of the penetrated sand. The strength of the bond formed is due to the mechanical interlocking of the irregular metal surface and the solidified slag.



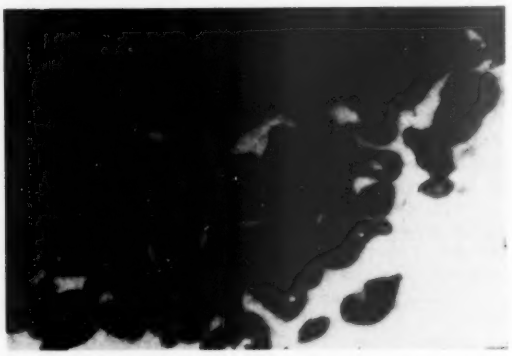
a. Early stage of oxidation. Formation of internal oxide particles, relatively smooth surface.



b. Formation of some surface pits. Increase in size and number of oxide particles in metal.



c. Linking up of oxide particles and surface pits. Increased roughening of surface.



d. Destruction of original prongs formed and further pitting of surface.

Figure 2—Stages in the formation of an irregular metal/oxide interface by oxidation of an originally smooth surface (Manganese steel). 500x

Summarized Conclusions

The investigation has clearly demonstrated that reactions occurring *after* metal solidification are important in sand adherence to steel castings. The major conclusion is that adherence of non-metallic, low-melting point refractory materials to solid iron and steel surfaces is due to mechanical causes, i.e., the interlocking of the two materials. The interatomic forces which act across a smooth metal-slag interface at elevated temperatures are evidently not sufficiently strong in themselves to maintain adherence between metal and slag when differential contraction occurs on cooling. However, the importance of the pitted and pronged metal surface produced by oxidation and the subseqent oxide-refractory interactions in promoting sand adherence to the metal surface has been shown. Because of the essential part played by oxidation in modifying the surface of the heated metal, it is logical to restrict the term "burn-on" to describe this adherence of mold materials without metal penetration. The conditions which are necessary to produce burn-on are summarized as follows:

1. Burn-on can occur only after solidification of the metal.
2. Oxidation of the metal must produce a pitted and pronged surface.
3. A liquid slag phase with a lower melting point than that of the metal, which will wet the metal (and the sand) must come into contact with the roughened metal surface, and it, or previously formed metal oxide, must penetrate between the sand grains by capillarity.
4. Solidification of the liquid phase must produce a mechanically strong bonding material which will not break away from the metal surface on cooling further.

If liquid slag is present at the liquid metal surface and remains in contact with the metal while it solidifies, oxidation of the metal surface is prevented until the slag solidifies and separates from the metal. Production of an oxidized metal surface after this stage does not cause adherence since all the phases present are now in the solid state. Even if the slag is an oxygen carrier, oxidation of the metal surface is slowed down and may not be sufficient to form a sufficiently roughened surface (this point has been demonstrated by the melting of fayalite on a polished iron surface in a neutral atmosphere subsequently made oxidizing). Some of the clean peels which have resulted in experiments on mold washes were undoubtedly due to the formation of slag while the metal was still molten.

The present results may be used to enlarge the general picture of phenomena occurring in a sand mold after metal has been cast.

During pouring, a thin, solid, chilled layer is first formed adjacent to the mold surface. If the temperature and thermal capacity of the unsolidified metal are sufficiently high, this skin remelts, but if it does not, the close contact between the sand and the metal may lead to burn-on by the mechanism outlined. In the case of remelting, if the metallostatic pressure is not high enough to cause penetration of the metal into the pores of the mold, final solidification is accompanied by the formation of a contraction gap between the metal and mold. The hot, solidified casting is not entirely separated from the mold by this gap, but is supported at various points: here, close contact of mold and hot metal leads to the possibility of burn-on of the mold material. Probable areas of close contact are the base of the casting and any horizontal fins or arms. Some of these susceptible areas are the areas which are prone to metal penetration. Undoubtedly, the two mechanisms of sand adherence may be operative in the same casting.

If air and water vapor are prevented from reaching the metal surface at the points of contact, burn-on does not occur. Good results have in fact been achieved in foundry practice by using graphitic mold washes which maintain a reducing atmosphere. The presence of a fluid slag layer at the hot surface can also prevent oxidation and lead to the desirable "glassy" peel; but this slag layer must be formed *before* the metal solidifies in order to maintain a smooth unoxidized surface which will strip easily. Certain liquid-forming mold washes, therefore, may be expected to prevent burn-on, in addition to forming a barrier to penetrating metal. The use of a sand or mold wash which does not react with iron oxide to give a strong bonding material should also assist clean peeling of the casting from the mold: the usually good results of zircon sands and washes in practice are probably to be thus explained.

Savage and Taylor[11] state that more severe sand adherence is found with small, thin castings than with large ones. This is to be expected, because remelting of the surface skin is not so likely to occur with small castings and the condition of much close contact of hot solid metal leading to burn-on may well be present. Similar conditions may prevale if metal is poured at too low a temperature. As the size of castings increases, burn-on may tend to become more localized, but, of course, sand adherence caused by metal penetration becomes more likely.

Preventative factors may be fortuitous (e.g., the formation of a contraction gap) or they may be planned (e.g., in the use of a mold wash) and, although it is not yet possible to predict from theoretical considerations how far each may assist in the alleviation of burn-on, the picture of the reactions given above may indicate what steps might be taken to prevent burn-on in a particular case. For example, with a small casting, an increase of casting temperature, the choice of a suitable mold wash, or use of a sand that does not react with the metal oxide to give a strong bonding material, might be separately or together sufficient to eliminate burn-on. The picture is by no means complete, and much more additional information on mold-metal reactions is desirable.

RUSSIAN PRODUCTION OF STEEL CASTINGS IN METAL PERMANENT MOLDS

According to a recently translated Russian textbook,* the production of steel castings of many sizes and shapes by the use of permanent molds has become well established and is continually finding wider application in many Soviet works. The process described is one in which steel or grey cast iron molds, or mold sections, are reportedly used in conjunction with sand cores, covers and runners to produce steel casting of high solidity and yield. More economical and successful casting can be produced if only a small part of the casting lies in the metal mold and the remainder is molded in sand. The following is an extended summary of the procedure and recommendations contained in the textbook.

*"Kokillenguss-Herstellung von Grauvnd Stahlformguss in Metallischen Dauerformen", A. M. Petritschenko. (German translation of original Russian book)

Casting and Mold Design

Castings which vary widely in weight, shape and dimensions can be produced in permanent molds, but, of course, simple, thick-walled castings are more easily produced than complicated, thinner ones. Projecting edges of the molds melt away very quickly in contact with the molten steel, and stresses developed by the wide difference in temperature between the outer and inner walls of the mold (750 - 1470 degrees F) cause the mold to fracture. Thus the design of the metal mold must be as simple as possible, and sand cores should be designed and applied so that casting complexities are contained in the cores rather than in the metal mold. It is considered better to use half-molds, or to change the design of the article, than for the mold to have a complicated structure. Often only slight changes in the structure of the article make it possible to use quite simple molds.

The molds are usually made in one piece with no divisions and the upper part of the mold, covering the casting, consists of a sand core. However, some castings have been successfully produced in split molds. The life of the upper portion of such a mold is almost 50 percent less than that of the lower portion. Molds split vertically are only used for the permanent mold casting of steel in special cases.

It is essential that any sharp projecting edges or corners in the mold be rounded, the radius of curvature of the rounded edge increasing with the wall thickness of the casting at the point of contact with the projection. The stream of molten metal should not be directed against any projection in the mold, or the projection will be broken by the metal after only a few pourings.

The use of one-piece permanent molds containing several casting cavities is not recommended, for a defect in any of the casting cavities would necessitate the rejection of the entire unit. It is best to use single molds assembled into groups before pouring. Such an assembly is shown in Figure 1 and is assembled as follows:

The single molds, cast in one piece, are placed on a mild steel or grey cast iron turnover plate according to a template. The upper cores, carrying a common pouring system and covering the molds, are connected together and placed on top. This enables all the molds on the plate to be filled simultaneously with a single pouring cup and runner so that the total capacity of the molds is much greater than that of a single mold, thereby facilitating the use of large ladles. Such a mold assembly has a much longer life than a multiple mold of the same size but cast in one piece. An added advantage is the fact that each mold can be rotated on its axis; so that the same part of the mold need not always be subjected to the full force of the molten metal flowing into the mold.

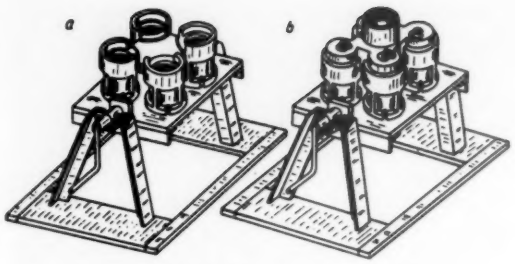


Figure 1—Mold assembly for group casting.

a. Setting up molds on the plate.

b. Mold assembly with cover core in place, ready for casting.

Technique of Producing Steel Castings in Permanent Molds

The most important factor in the production of steel castings in permanent molds is the preparation of the mold itself. The molds must be free of rust, residual mold wash from previous use and cracks or ruptures. The molds should be cleaned while hot with a wire brush and sandblasted occasionally to remove rust and old mold wash from any slight erosions or irregularities. Slightly defected molds must be sandblasted more often and inspected carefully.

The molds are then coated with a refractory wash, silica flour, graphite or chromic oxide washes are recommended. The wash should be applied while the molds are still hot from previous use (212 - 480 degrees F). However, the coating of molds at temperatures over 570 degrees F is not recommended, since the coating will then dry too quickly, leaving a rough and uneven surface. A coating applied to molds which are too hot may spall, thereby producing a defective casting. Particular attention must be given to the coating of eroded or otherwise slightly defected molds.

The molds are preheated to 170 - 390 degrees F before pouring in order to: (1) reduce the severity of the chill effect, which is particularly important for thin section castings; (2) dry the mold wash if it has been applied to a new, cold mold, and (3) to eliminate the deposition of moisture on the inner walls of the mold, which might lead to cracking of the mold and/or casting. Special attention must be given to the preheat of the molds, since the long intervals between the pourings of steel allow the molds to cool too much to be used without preheating. Preheating is accomplished with the aid of burners or portable coal-heated mold driers or by placing the last hot castings into the reassembled molds.

The molds should be assembled just before they are to be poured, cleaned and blown out with air, and inspected carefully. The assembly procedure should be carried out at or very near the pouring

area to take advantage of the residual heat in the molds from the last pouring.

The metal should be poured in a smooth, uninterrupted stream. All spill-over burrs must be removed at once and the mold unloaded and dissembled. The castings should not be removed from the molds until they are completely solidified, but must be removed as soon as possible to reduce the cracking tendency. The optimum length of time from each casting to remain in the mold after casting must be determined experimentally in each case.

Types of Defects and Their Prevention

CRACKS—Most rejects in permanent mold castings are caused by hot tearing. The number of rejects from this cause, in the production of complicated thin-walled castings, is usually very large at first, but can usually be reduced as experience is gained. Cracking and hot tearing is, of course, effected by the metal itself, the design and hindrance of contraction, and these factors must be considered in the elimination of cracking.

The condition and design of the mold, the collapsibility of the sand cores and the time at which the casting is removed from the mold are the most important factors to be considered. The mold should be so designed, prepared and assembled as to eliminate any burrs or projections which would hinder the contraction of the casting, and the cores must be as yielding as possible. Good results can be obtained with dried oil cores, but lean mixtures or hollowed cores should be used to improve the collapsibility. Green cores are also used for their collapsibility.

Cracking can, therefore, be prevented in the following ways:

a) no molds must be used in which the free contraction of the casting is prevented;

b) the mold clamps should be released at the right moment after casting;

c) the castings should be removed from the molds as soon as possible;

d) the steel should be poured at a high temperature;

e) the molds should always be heated before casting;

f) easily yielding cores should be used (cores with cavities, made out of yielding material, etc.);

g) no steel with excessively high gas content should be poured;

h) attention should be paid to the accurate assembly of the molds, in order to avoid burrs;

i) the use of cracked molds should be avoided.

GAS CAVITIES—The second most frequent cause of rejects in the permanent mold casting of steel is porosity. Porosity in the permanent mold casting of steel may be due, in some cases, to insufficiently dried or insufficiently permeable cores. Cavities due to these causes are distinguished from other types because they are situated on the surface of the casting facing the core. Preventive measures are: increased control of the quality of the cores, better drying of the cores, use of a core mixture with minimum gas evolution, good gas permeability, and improvement in the ventilation of the cores.

Gas porosity may also be caused by poor coating of the molds, inadequate drying of coated molds and insufficient preheating. Porosity blisters produced by the mold wash are unevenly distributed over the casting, and are frequently open. Porosity of this type can be avoided by using a suitable mold coating and by heating the mold after coating, before casting.

Another cause of porosity in steel permanent mold castings is the use of rusty, badly cleaned molds. The most difficult places in the molds to clean are those where there are slight erosions and small cracks arising during operation. Scale and rust collect in these spots, and give rise to porsity, particularly when the protective coating on the inner face of the mold is thin.

MISRUNS—Rejects are often caused by incomplete filling of the mold. This may occur when the casting temperature is too low, when the metal is cast into cold molds, or when casting is too slow or is interrupted.

The other types of defects occurring in the permanent mold casting of steel (slag inclusions, inaccurate casting, etc.) are no different from the defects which occur in ordinary casting, and need not be mentioned here.

Summary

The following recommendations for producing steel castings in permanent molds should be observed:

1. Castings and molds should be designed as simply as possible. The main part of the outer contours of the casting should be formed by the wall of the mold itself. The casting should always be designed as simply as possible.

2. Split molds, particularly vertically-split molds and those with removable parts, should be avoided.

3. For small and medium castings, mold assemblies should be used in place of multiple molds cast in one piece.

4. Half-molds should be used to produce complicated and thin-walled castings. Care must be taken to see that the castings can contract freely on solidification.

5. The pouring system should always be situated in the cores, or pouring cups of a refractory

material should be used. The molten metal stream should not be directed against the mold wall.

6. The inner walls of the mold should not be machined, as the life of the mold is considerably lengthened by an undamaged casting "skin".
7. Vents and risers should always be placed in the cores. Closed risers are better than open.
8. Sharp edges and projections in the mold should be avoided, as they rapidly render the mold unusable.
9. The casting should be so arranged in the mold that the thick-walled parts lie uppermost, to avoid shrinkage pipes. If necessary, the upper part of the casting may be placed in the core.
10. The gating system should, if possible, be arranged so that the place where the metal enters the mold may be changed from time to time.
11. In making large and fairly large thick-walled castings, steel molds should be used in place of grey cast iron.

The following precautions should be taken in making thin-walled permanent mold castings: the steel should be poured at a higher temperature and poured rapidly, molds should be pre-heated, top-pouring should be used, the metal should rise as rapidly as possible in the mold and the steel should be carefully deoxidized. The thinner the casting, the more carefully must all these provisions be carried out. Further special precautions must be taken in making complicated thin-walled castings. Hubs and pulleys with walls only $\frac{1}{4}$ - $\frac{5}{16}$ inch thick have been successfully produced with such precautions.

VIBRATION TECHNIQUE FOR CASTING STEEL

A recent Polish publication disclosed the interesting results of a Polish evaluation* of a dynamic or vibration technique for producing steel castings. The experiments were designed to determine the effect of vibrating the mold during the pouring and solidification of the metal on the mechanical properties of the steel and the quality of the resultant casting. The tests were divided into (1) laboratory experiments, in which an attempt was made to evaluate general applicability of the technique, and (2) production of castings under actual foundry conditions. Two castings were made in all cases: one under the normal static conditions and the other using the vibrating casting technique. The results obtained for the two types of casting were compared with particular reference to differences in (1) chemical analyses, (2) mechanical properties, for example, tensile strength and hardness, and (3) microstructure.

No striking improvements were noted in the mechanical properties, although all cast specimens solidifying under vibration technique showed higher and more uniform values as compared with statically cast products. In addition, no blow holes were noted in the vibrated castings while this defect occurred in the castings produced in the usual way.

The equipment for vibrating the molds consisted of a platform supported on four springs and vibrated by an eccentric weight mounted on a shaft driven at 1,440 r.p.m.

The laboratory evaluation of the technique was followed by attempts to produce wheels for railway trucks, parts for railway locomotives, etc. It soon became obvious after a few unsuccessful castings were obtained that vibrating the mold during the pouring stage is impracticable; the practice was then modified so that the vibrator began operating only after the pouring was complete. A 5 degree tilt was given to the platform of the vibrator as a further improvement, and the mold was so arranged that the pouring basin was located over the highest point of the platform. Several changes in the gating system had to be made before a railway truck wheel was successfully cast. Further castings were then made with very good results.

The effect of this vibrating technique on the macro- and microstructure of steel and on the occurrence of porosity was studied as a further step in evaluating the method. These castings were subsequently tested for leaks at pressures up to 40 atmospheres (60 psi). The results show that in the case of statically produced castings, about 30 percent of all castings had to be rejected because of internal cracks and porosity, which made them unsuitable for high pressure duties. The same type of castings produced with the aid of the vibrators stood up well to tests at 40 atmospheres pressure.

This new technique compares favorably with other means of improving the yield and the quality of castings without the necessity of heavy capital investment. The vibrating technique of casting is not an answer to all casting defects; however, it is capable of diminishing the percentage of foundry scrap caused by porosity, internal blowholes and other defects caused by faults in the moldmaking and in the steelmaking practices. Porosity-free structure of the castings produced by the method indicates its possibilities in the manufacture of all types of machine parts, etc., where air-, gas- and water-tightness are of primary consideration.

*"Dynamic Method of Casting", H. Mastalerz, Przeglad Odlewnictwa, 2, July-August, 1952, p. 233.